

5 **Title: COMPOSITIONS COMPRISING A DISPERSANT AND AN
OVERBASED CARBOXYLATE OR SULFONATE FOR
RHEOLOGY CONTROL IN COATINGS & INKS**

SUMMARY OF THE INVENTION

A mixture of a calcium overbased carboxylate or sulfonate and a dispersant provides rheology control in various resin and pigment containing organic media. 10 These compositions can influence the flow properties under high shear and/or elevated temperatures than non-modified compositions.

BACKGROUND OF THE INVENTION

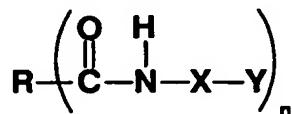
15 When applying coatings that contain a high amount of solids such as industrial coatings, maintenance coatings or paints, there is a tendency for the coating to sag or run if the viscosity is not controlled. This tendency is especially prevalent when a workpiece, which is to accept the coating, is in a vertical position. Regarding workpieces that are vertically oriented, the coating may droop or sag due to gravity so that the final film thickness of the coating is uneven. Some sagging 20 may occur by influence of gravity when the coating is applied. However, such sagging is more particularly a problem when baking the applied coating. An approach to overcome the sag problem is to include a rheology control agent in the coating. Such rheology control agents basically cause the coating to be shear thinning and to have high viscosity (decreased fluidity) at low shear while providing 25 sufficiently low viscosity at high shear to permit flow and leveling on the workpiece.

30 U.S. Patent No. 4,451,597 (Victorius, May 29, 1984) relates to coating composition useful as the exterior finish on automobiles and trucks and contains about 25-50% by weight of a binder of film-forming constituents and 50-75% by weight of a volatile organic solvent carrier and additionally contains 2-150% by weight, based on the weight of the binder, of pigment; the binder is about 20-70% by weight of an acrylic polymer containing reactive hydroxyl, carboxyl, amide groups or any mixture of such groups, about 0-40% by weight of a hydroxy-terminated polyester urethane resin and about 25-40% by weight of an alkylated melamine formaldehyde crosslinking resin; in addition the composition contains about 4-20%

by weight, based on the weight of the binder, of a rheology control agent of an alcohol soluble cellulose acetate butyrate having a butyl (sic) content of about 40-50% by weight, a hydroxyl content of about 4-5% by weight and a viscosity of about 0.2-0.4 second.

5 U.S. Patent No. 5,034,444 (Yun et al., July 23, 1991) discloses a rheology additive for non-aqueous coating compositions. The additive may be the reaction product of an alkoxylated aliphatic nitrogen-containing compound, an aliphatic diamine or mixtures thereof, and an organic polycarboxylic anhydride or acid, an alkanediol polyepoxide ether, or mixtures thereof. The additive provides excellent
10 anti-sag and storage stability properties, particularly for high solids coating compositions, without causing a significant increase in viscosity. Also disclosed are coating compositions containing the additive.

15 U.S. Patent No. 5,086,104 (Wada et al., February 4, 1992) discloses polyester resin compositions which include a crystalline thermoplastic polyester resin (such as polybutylene terephthalate), a polyester elastomer (such as a copolymer including recurring hard and soft segments) and between 0.005 to 10 parts by weight, based on 100 parts of the crystalline and elastomeric resins, of an amide compound having the formula



20 wherein R is an organic group such as an aromatic ring, X is an alkylene of C₂ to C₁₀ such as ethylene and propylene, Y is -COOH, -OH, -SH or -NH₂ and n is 2 to 4, inclusive.

25 U.S. Patent No. 4,321,098 (Lal, June 14, 1994) relates to a composition mixture comprising (i) at least one ester-acid, ester-salt or mixtures thereof and (ii) at least one amidic-acid, amidic-salt or mixtures thereof and polymer fabrics treated with the same. The treated polymer fabrics have improved wicking-wetting characteristics. The treated polymer fabrics maintain these characteristics upon repeated exposure to aqueous fluids.

30 U.S. Patent No. 5,369,184 (Burgoyne, Jr. et al., November 29, 1994) relates to resins which comprise polymers which contain multiple acetal groups that have

been developed which are useful for crosslinking and adhesion promotion in coating and adhesive applications. The polymers which make up these resins are prepared by the addition of aminoacetals to polymers containing anhydride functionality. The polymers are modified by titration with ammonia or a primary or secondary amine which solubilizes the polymer in aqueous systems.

5 U.S. Patent No. 5,374,682 (Gouda et al., December 20, 1994) is directed to a thermosetting coating composition that contains (a) an acrylic resin having hydroxyl groups and epoxy groups in a molecule thereof; (b) a resin prepared from a monomer having an unsaturated group and an acid anhydride group the acid anhydride group being half-esterified, half-thioesterified and/or half-amidized; (c) at least one of hydroxyl group-containing resin selected from the group consisting of an acrylic resin containing hydroxyl groups and carboxyl groups, a fluorine-containing copolymer resin and a polyester resin; and (d) a melamine resin.

10 U.S. Patent No. 5,536,871 (Santhanam, July 16, 1996) is directed to a liquid, pourable rheology additive especially useful for thickening liquid organic compositions which comprises the reaction product of a defined polyalkoxylated nitrogen-containing compound, polycarboxylic acid and a liquid diamine. The additive, which exists in a pourable, pumpable form at up to a 100% rheologically active composition, exhibits excellent thickening efficiency for systems including inks, epoxies, polyesters, paints, greases and other systems, including ease of dispersibility, without adversely affecting gloss. The additive operates by both an associative and a reaction mechanism to provide rheology properties to such systems, and is also similarly useful for aqueous systems.

15 Printing inks are a special class of coatings formulated to transfer and reproduce an image from a printing surface (plate or cylinder) to a substrate such as paper or plastic, etc. These inks consist of various pigments or colorants in a varnish which is typically a film former consisting of various resins, solvents, and other additives, so that the resulting fluid will distribute and transfer on to the printing press. Lithographic and letterpress inks are higher viscosity formulations often referred to paste inks. Most modern litho ink presses run at speeds of 1500-2000 feet per minute but are capable of running to up to 3000 feet per minute. As one

would expect the temperature of the ink increases as speed increases and this affects the operating window under which the press can perform satisfactorily. Therefore, inks must be formulated to run under wide variations of conditions, to minimize the change in viscosity as a function of temperature. The viscosity of a fluid is generally 5 dependent upon temperature among other factors. As the temperature of the fluid is increased, the viscosity usually decreases, and as the temperature is reduced, the viscosity usually increases. One of the functions of a rheology control agent for the purpose of this invention is to reduce the extent of the decrease in viscosity as the temperature is raised or to reduce the extent of the increase in viscosity as the 10 temperature is lowered. Such rheology control agents in motor oil applications are generally usually polymeric materials and are often referred to as Viscosity Index improvers. Thus, a viscosity improver ameliorates the change of viscosity of system containing it with changes in temperature. In inks it is highly desirable that the rheology control agents do not adversely affect the low/ ambient temperature 15 viscosity of the formulations containing same. Frequently, the rheology control agents simply act as thickeners to enhance the high temperature properties. Accordingly, it is desirable to provide compositions that reduce the extent of loss of viscosity at high temperatures while not adversely increasing the low temperature viscosity of inks.

20

U. S. patent 3,819,386 (Higgins, June 25, 1974) is directed to the usage of an alkaline earth metal salt of a fatty acid and a dispersant to act as thickeners and to provide plastic flow to printing inks.

25

DETAILED DESCRIPTION OF THE INVENTION

Overbased additives have been known for a long time. They have been used extensively as industrial lubricants in engines, gears and other industrial applications. Specifically they have been used as detergents, extreme pressure and antiwear agents, anticorrosion and antirust additives, and as rheology control agents 30 in coatings. They are metal salts of acidic organic compounds. Overbased materials are single phase, homogenous, and generally apparently Newtonian systems

characterized by a metal content in excess of that which would be present according to the stoichiometry of the metal and the particular acidic organic compound reacted with the metal. Overbasing, also referred to as superbasing or hyperbasing, is a means for supplying a large quantity of basic material in a form which is soluble or dispersable in organic medium. Overbased products have been long used in lubricant technology to provide detergent additives.

Overbased materials are generally prepared by reacting an acidic material, normally an acidic gas such as SO₂ or CO₂, and most commonly carbon dioxide, with a mixture comprising an acidic organic compound, a reaction medium normally comprising an oleophilic medium, a stoichiometric excess of a metal base, and preferably a promoter.

The amount of excess metal is commonly expressed in terms of metal ratio. The terminology "metal ratio" is used in the prior art and herein to designate the ratio of the total chemical equivalents of the metal in the overbased materials (e.g., a metal sulfonate or carboxylate) to the chemical equivalents of the metal in the product which would be expected to result in the reaction between the organic material to be overbased (e.g., sulfonic or carboxylic acid) and the metal-containing reactant (e.g., calcium hydroxide, calcium oxide, etc.) according to the known chemical reactivity and stoichiometry of the two reactants. The actual stoichiometric excess of metal can vary considerably, for example, from about 0.1 equivalent to about 30 or more equivalents depending on the reactions, the process conditions, and the like. Obviously, if there is present in the material to be overbased more than one compound capable of reacting with the metal, the "metal ratio" of the product will depend upon whether the number of equivalents of metal in the overbased product is compared to the number of equivalents expected to be present for a given single component or a combination of all such components. The methods for preparing the overbased materials as well as an extremely diverse group of overbased materials are well known in the prior art and are disclosed for example in the following U.S. Pat. Nos.: 2,616,904; 2,616,905; 2,616,906; 2,616,911; 2,616,924; 2,616,925; 2,617,049; 2,695,910; 2,723,234; 2,723,235; 2,723,236; 2,760,970; 2,767,164; 2,767,209; 2,777,874; 2,798,852; 2,839,470; 2,856,359; 2,859,360; 2,856,361; 2,861,951;

2,883,340; 2,915,517; 2,959,551; 2,968,642; 2,971,014; 2,989,463; 3,001,981; 3,027,325; 3,070,581; 3,108,960; 3,147,232; 3,133,019; 3,146,201; 3,152,991; 3,155,616; 3,170,880; 3,170,881; 3,172,855; 3,194,823; 3,223,630; 3,232,883; 3,242,079; 3,242,080; 3,250,710; 3,256,186; 3,274,135; 3,492,231; and 4,230,586.

5 These patents disclose processes, materials which can be overbased, suitable metal bases, promoters, and acidic materials, as well as a variety of specific overbased products useful in producing the disperse systems of this invention and are, accordingly, incorporated herein by reference.

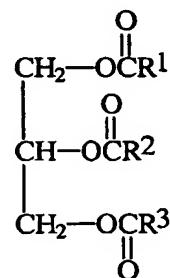
10 Within this preferred group of overbased carboxylic and sulfonic acids, the calcium overbased mono-, di-, and tri-alkylated benzene and naphthalene (including hydrogenated forms thereof), and higher fatty acids are especially preferred. Illustrative of the synthetically produced alkylated benzene and naphthalene sulfonic acids are those containing alkyl substituents having from about 8 to about 30 carbon atoms, preferably about 12 to about 30 carbon atoms, and advantageously about 24 15 carbon atoms. Such acids include di-isododecyl-benzene sulfonic acid, wax-substituted phenol sulfonic acid, wax-substituted benzene sulfonic acids, polybutene-substituted sulfonic acid, cetyl-chlorobenzene sulfonic acid, di-cetyl-naphthalene sulfonic acid, di-lauryldiphenylether sulfonic acid, di-isonylbenzene sulfonic acid, di-isoctadecylbenzene sulfonic acid, stearyl 20 naphthalene sulfonic acid, and the like.

25 The carboxylic acid of the present invention can include both saturated and unsaturated carboxylic acid of 8 to 30 carbon atoms or reactive equivalents of said carboxylic acids. The phrase "reactive equivalent" of a material means any compound or chemical composition other than the material itself which reacts or behaves like the material itself under the reaction conditions. Thus reactive equivalents of carboxylic acids will include acid-producing derivatives such as anhydrides, alkyl esters, triglycerides, acyl halides, lactones and mixtures thereof unless specifically stated otherwise. It is to be noted that a reactive equivalent of a carboxylic acid as aforementioned, such as a triglyceride may itself contain carbon atoms in excess of the preferred range of 8-30 in that the triglyceride has three ester 30 functionalities formed by reacting three moles of a carboxylic acid with one mole of

glycerol. The range of carbon numbers given above therefore refers only to the carboxylic acid, and not to the total carbon atoms of any reactive equivalent.

Examples of useful carboxylic acids include but are not limited to caprylic acid, capric acid, lauric acid, myristic acid, myristoleic acid, decanoic acid, 5 dodecanoic acid, pentadecanoic acid, palmitic acid, palmitoleic acid, margaric acid, stearic acid, 12-hydroxystearic acid, oleic acid, ricinoleic acid, linoleic acid, linoleic acid, arachidic acid, gadoleic acid, eicosadienoic acid, behenic acid, erucic acid, mixtures of any of these acids or their reactive equivalent.

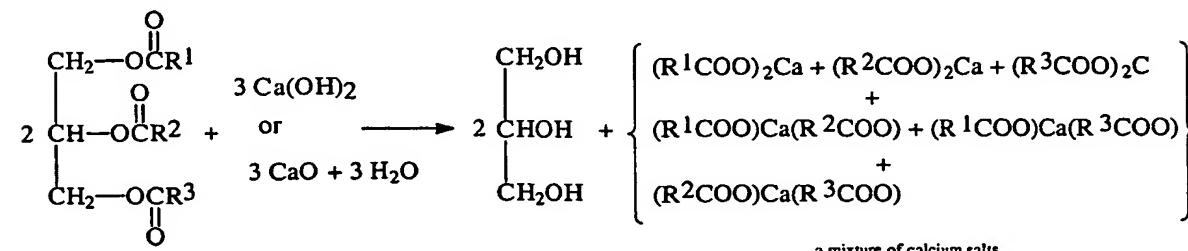
The carboxylic acid or its reactive equivalent can also comprise at least one 10 natural oil comprising an animal oil or vegetable oil comprising a triglyceride of the formula



wherein R¹, R² and R³ are independently hydrocarbyl groups containing 7 to 29 carbon atoms. Examples of suitable vegetable oils include coconut oil, soybean oil, 15 tall oil, tung oil, rapeseed oil, sunflower oil, including high oleic sunflower oil, lesquerella oil and castor oil.

The calcium base of the present invention is selected from the group consisting of calcium oxide (CaO) and calcium hydroxide (Ca(OH)₂).

When the carboxylic acid present in the form of a reactive equivalent such as 20 a triglyceride is initially reacted together with the calcium base, hydrolysis of the triglyceride takes place to form a saponified intermediate.



The equivalent ratio of the calcium base to the carboxylic acid is between 2:1 and 10:1; thus sufficient calcium base is present to effect saponification quantitatively (i.e. 100%). When the saponified intermediate is obtained, glycerol is also formed. It is important to note that this system differs from the prior art in that 5 no free glycerol is added at the beginning of the saponification reaction. The glycerol formed, although not considered to be a "promoter" (a term discussed below), can aid in the incorporation of the excess calcium in the overbasing process. It can act as both a diluent and contact agent and remains within the composition.

The carbonation of the mixture of (I) takes place through the use of carbon 10 dioxide, an acidic gas. The amount of carbon dioxide which is used depends in some respects upon the desired basicity of the product in question and also upon the amount of calcium base employed, which as discussed above will vary (in total amount) from 2-10 equivalents per equivalent of carboxylic acid. The carbon dioxide is generally blown below the surface of the reaction mixture of (I) along 15 with additional (i.e., amounts in excess of what is required to convert the carboxylic acid quantitatively to the calcium carboxylate salt) calcium base after the calcium carboxylate intermediate is formed. The calcium carboxylate intermediate is formed either from direct reaction of the carboxylic acid with the calcium base or through saponification of a reactive equivalent of the carboxylic acid, such as a triglyceride. 20 The process of carbonation which is a part of the process of overbasing is well known to those skilled in the art. The carbon dioxide employed during the carbonation step is used to react with the excess calcium base which may be already be present or which can be added during the carbonation step. The mixtures of products obtained after carbonation are referred to herein as overbased materials of 25 this invention which include calcium carbonate formed from the reaction of carbon dioxide and calcium hydroxide.

The carbonation is carried out in the presence of a promoter. Promoters are chemicals which can be employed in the overbasing process to facilitate the incorporation of the large excess metal into the overbased compositions. Typical 30 examples of promoters used in overbasing include water; phenolic materials such as phenol; alcohols of various kinds, such as methanol, 2-propanol, the butyl alcohols,

the amyl alcohols, as well as mixtures of alcohols; mono-glycerides; di-glycerides; and amines such as aniline and dodecyl amine. The promoter system used in the present invention consists of a mixture of water and an alcohol of 1 to 8 carbon atoms. The alcohol can preferably be selected from the group consisting of 2-propanol (isopropyl alcohol), 1-butanol, and 2-methyl-1-propanol (isobutyl alcohol).
5 In a more preferred embodiment, the alcohol is 2-methyl-1-propanol.

These ordinary overbased materials can be gelled, i.e. converted into a gel-like or colloidal structure, by homogenizing a "conversion agent" with the overbased starting material. "Ungelled" overbased materials are normally Newtonian materials
10 which are homogeneous on a macroscopic scale. Gelled overbased materials are well known materials. They can be converted from their original Newtonian form to a gelled form by a variety of treatments. The details of the process are described in U.S. patents 3,492,231; 5,300,242 and 5,508,331.

The terminology "conversion agent" is intended to describe a class of very
15 diverse materials which possess the property of being able to convert the Newtonian homogeneous, single-phase, overbased materials into non-Newtonian colloidal disperse systems. The mechanism by which conversion is accomplished is not completely understood. However, with the exception of carbon dioxide, these conversion agents generally possess active hydrogens. The conversion agents
20 generally include lower aliphatic carboxylic acids, water, aliphatic alcohols, polyethoxylated materials such as polyglycols, cycloaliphatic alcohols, arylaliphatic alcohols, phenols, ketones, aldehydes, amines, boron acids, phosphorus acids, sulfur acids, and carbon dioxide (particularly in combination with water). Mixtures of two or more of these conversion agents are also useful. Particularly useful conversion
25 agents are alcohols having less than twelve carbon atoms while the lower alcohols, i.e., alcohols having less than six carbon atoms, are preferred for reasons of economy and effectiveness in the process.

The use of a mixture of water and one or more of the alcohols is known to be especially effective for converting the overbased materials to colloidal disperse
30 systems and is used as the conversion agent in the instant invention. For the present invention, the preferred alcohols are selected from the group consisting of 2-

propanol, 1-butanol, 2-methyl-1-propanol and mixtures thereof, with the most preferred being 2-methyl-1-propanol (isobutanol). Thus the same alcohols used during carbonation can also be used in the gelation step. In one embodiment, a mixture of water and 2-methyl-1-propanol is used in the gelation step. The details of 5 the process are described in U.S. patents 3,492,231; 5,300,242 and 5,508,331, 5,401424, and 5,919,741.

Removal of volatile materials need not be limited to removal of the conversion agents, however. It is possible, for instance, to completely isolate the solid components of the gelled material as dry or nearly dry solids. (In this context 10 the term "solid" or "solids" includes not only sensibly dry materials, but also materials with a high solids content which still contain a relatively small amount of residual liquid.) Isolation of solids can be effected by preparing the composition in an oleophilic medium which is a volatile organic compound. The term "volatile" as used in this context describes a material which can be removed by evaporation. 15 Xylenes, for example, would be considered volatile organic compounds. Heating of the gel to a suitable temperature and/or subjecting it to vacuum can lead to removal of the volatile oleophilic medium to the extent desired. Typical methods of drying include bulk drying, vacuum pan drying, spray drying, flash stripping, thin film drying, vacuum double drum drying, indirect heat rotary drying, and freeze drying. 20 Other methods of isolation of the solids can also be employed, and some of those methods do not require that the oleophilic medium be a volatile material. Thus in addition to evaporation, such methods as dialysis, precipitation, extraction, filtration, and centrifugation can be employed to isolate the solid components of the gel.

The solid material thus isolated may be stored or transported in this form and 25 later recombined with an appropriate amount of an oleophilic medium. The redispersion into oil can be accomplished more readily when the solid material is not dried to absolute dryness, i.e. when a small amount of solvent remains in the composition. Alternatively an appropriate amount of an oil such as a mineral oil, a natural oil such as vegetable oil, e.g., coconut oil or the like, or synthetic oil, or a 30 surfactant, can be present in the nominally dry powder to aid in dispersion. The solid materials, when dispersed in an appropriate medium, can provide a gel, a

coating composition, a grease, another lubricant, or any of the materials which can be prepared from the originally gelled material. The solid materials can also be used without redispersion for their intrinsic lubricating properties.

The oleophilic medium used for preparing and containing overbased materials will normally be an inert solvent for the acidic organic material. The oleophilic medium can be an oil or an organic material which is readily soluble or miscible with oil. The organic material can include an organic solvent which can include both aliphatic and aromatic organic solvents and mixtures thereof.

In one embodiment, the organic solvent comprises such materials as mineral spirits and Stoddard Solvent. Mineral Spirits is often referred to as Heavy Naphtha. It has high flash point and solvent power and is extensively used in coatings industry. In another embodiment of the invention, the organic solvent is a petroleum middle distillate fraction such as those available from Magie Bros. Oil Company under the trade name Magie Sol, or from Exxon Chemical under the trade name Exxprint, etc. Such distillates are extensively used in lithographic inks and are typically aliphatic hydrocarbons with limited aromatic character and vary in boiling range from 200 C- 350 C.

Suitable aromatic solvents include benzene, alkylbenzenes, high flash solvent naphtha, and mixtures thereof. Alkylbenzene includes toluene, xylenes and ethylbenzene as well as benzene rings having different alkyl groups attached thereto, such as methyl ethyl benzene, and mixtures thereof. In one embodiment, the aromatic solvent is SC 100 solvent, which is made up almost entirely of aromatics, comprising mostly high boiling toluenes.

It is also possible to remove the water and alcohol present in the overbased mixture and add a diluent (such as an oil, organic solvent, or vegetable oil) which may be the same or different from the diluent used during overbasing.

Definitions

As used herein, the term "hydrocarbyl substituent" or "hydrocarbyl group" is used in its ordinary sense, which is well-known to those skilled in the art. Specifically, it refers to a group having a carbon atom directly attached to the

remainder of the molecule and having predominantly hydrocarbon character. Examples of hydrocarbyl groups include:

(1) hydrocarbon substituents, that is, aliphatic (e.g., alkyl or alkenyl), alicyclic (e.g., cycloalkyl, cycloalkenyl) substituents, and aromatic-, aliphatic-, and alicyclic-substituted aromatic substituents, as well as cyclic substituents wherein the ring is completed through another portion of the molecule (e.g., two substituents together form an alicyclic radical);

(2) substituted hydrocarbon substituents, that is, substituents containing non-hydrocarbon groups which, in the context of this invention, do not alter the predominantly hydrocarbon substituent (e.g., halo (especially chloro and fluoro), hydroxy, alkoxy, mercapto, alkylmercapto, nitro, nitroso, and sulfoxo);

(3) hetero substituents, that is, substituents which, while having a predominantly hydrocarbon character, in the context of this invention, contain other than carbon in a ring or chain otherwise composed of carbon atoms. Heteroatoms include sulfur, oxygen, nitrogen, and encompass substituents as pyridyl, furyl, thienyl and imidazolyl. In general, no more than two, preferably no more than one, non-hydrocarbon substituent will be present for every ten carbon atoms in the hydrocarbyl group; typically, there will be no non-hydrocarbon substituents in the hydrocarbyl group.

The term "lower" when used in conjunction with terms such as alkyl, alkenyl, alkoxy, and the like, is intended to describe such groups that contain a total of up to 7 carbon atoms.

The term "water-soluble" refers to materials that are soluble in water to the extent of at least one gram per 100 milliliters of water at 25°C.

The term "oil soluble" refers to materials that are soluble in mineral oil to the extent of at least one gram per 100 milliliters of mineral oil at 25°C.

The term "total acid number" (TAN) refers to a measure of the amount of potassium hydroxide (KOH) needed to neutralize all of the acidity of a product or a composition. The sample to be tested is dissolved in a toluene and tert-butyl alcohol solvent and titrated potentiometrically with a solution of tetra-n-butylammonium hydroxide. The toluene and tert-butyl alcohol solvent is prepared by diluting 100 ml

of 25% methanolic tert-butyl alcohol and 200 ml of isopropyl alcohol to one liter total volume with toluene. The solution of tetra-n-butylammonium hydroxide is a 25% by weight solution in methyl alcohol. A Metrohm Standard pH Combination Glass Electrode EA 120 (3M aq. KCl), which is a combination glass-plus-reference electrode, is used. The end-points corresponding to the inflections are obtained from the titration curve and the acid numbers calculated.

The term "total base number" (TBN) refers to a measure of the amount of acid (perchloric or hydrochloric) needed to neutralize the basicity of a product or a composition, expressed as KOH equivalents. It is measured using Test Method 10 ASTM D 2896.

The number of "equivalents" of a hydrocarbyl substituted succinic acid or anhydride is dependent on the number of carboxylic functions (e.g., -C(=O)-) present in the acid or anhydride. Thus, the number of equivalents of acid or anhydride will vary with the number of succinic groups present therein. In determining the number 15 of equivalents of acid or anhydride, those carboxylic functions which are not capable of reacting with the polyol, polyamine or hydroxyamine (B) are excluded. In general, however, there are two equivalents of acid or anhydride for each succinic group in the acid or anhydride. Conventional techniques are readily available for determining the number of carboxylic functions (e.g., acid number, saponification 20 number) and, thus, the number of equivalents of the acid or anhydride available to react with component (B).

An "equivalent" of a polyol is that amount of polyol corresponding to the total weight of polyol divided by the total number of hydroxyl groups present. Thus, glycerol has an equivalent weight equal to one-third its molecular weight.

An "equivalent" of a polyamine is that amount of polyamine corresponding 25 to the total weight of the polyamine divided by the number of nitrogen atoms present which are capable of reacting with a hydrocarbyl substituted succinic acid or anhydride. Thus, octylamine has an equivalent weight equal to its molecular weight; ethylene diamine has an equivalent weight equal to one-half of its molecular weight. 30 The equivalent weight of a commercially available mixture of polyalkylene polyamines can be determined by dividing the atomic weight of nitrogen (14) by the

% N contained in the polyamine; thus, a polyalkylene polyamine mixture having a % N of 34 would have an equivalent weight of 41.2.

An "equivalent" of a hydroxyamine is that amount of hydroxyamine corresponding to the total weight of hydroxyamine divided by the number of hydroxyl groups and nitrogen atoms present which are capable of reacting with a hydrocarbyl substituted succinic acid or anhydride. Thus, diethanolamine has an equivalent weight equal to one-third its molecular weight.

The processes and compositions of the present invention can be used to prepare a variety of materials useful as additives for coating compositions, as stabilizing agents or additives for such compositions as polymeric compositions or for drilling muds or other down-hole oil field applications, as rheology control agents for water solutions, such as paints and invert emulsions, as lubricants (including greases) for oil field, automotive, steel mill, mining, railroad, and environmentally friendly applications, as lubricants for food-grade applications, metalworking, and preservative oils, as lubricants for abrasives (grinding aids), as a component of synthetic based invert lubricants, and in thermal stabilizer compositions for polymers such as polyvinyl chloride resin.

In a preferred embodiment, the overbased material prepared by the process of this invention can be used in a coating composition as a rheology control agent. Coating compositions include paints, certain inks, and various varnishes and lacquers. They often contain pigments in a dispersing medium or vehicle, a film-forming resin, and other conventional additives known to those skilled in the art. In inks, for example, typical resin is selected from at least one member of the group consisting of metal resinate, phenolic modified rosin, phenolic resin, hydrocarbon resin, hydrocarbon modified rosins, an acrylic resin, a polyamide resin, a maleic modified rosin, a fumaric modified rosin, and a cellulosic resin. Conventional coatings as well as high solid systems typically contain from 10 to about 50% by weight of non-volatile resins, such as those based on polyester-melamine, polyester-urea/formaldehyde, alkyd-urea/formaldehyde, acrylic-melamine, aryllic-urea/formaldehyde, epoxy resins, epoxy-ester-melamines, polyurethane resins, acrylic resins, oleoresins, unsaturated polyesters, polyvinyl acetates, polyvinyl

chlorides, or vinyl acrylics. Various other additives include additives for microbiological control (bactericides and fungicides), additives for fire retardance, additives that are inhibitors for rusting and corrosion, anti-gassing agents, additives for surface lubrication and mar and scuff resistance, anti-static agents, deodorants, 5 defoamers, antioxidants, gloss enhancers such as waxes, an anti-settling agent, and tannin stain suppressants.

In order to illustrate the invention, the following data is provided. It is understood, however, that the data is for illustrative purposes and are not intended to be limiting of the scope of the invention as set forth in the claims.

10

Table I
Effect of Dispersants on Stormer Viscosity and Sag Control in a White Paint Alkyd Formulation

	%Rheology Control Agents	Stormer Viscosity (D856)	Sag Test (D4400)
A	0.75% Overbased acid of Example 3A	73	9
B	0.75% Overbased acid of Example 3A 0.5% LZ 2174 (an alkyl aminoester according to this disclosure)	75	10
C	0.75% Overbased acid of Example 3A 0.5% PIBSA (a polyisobutylene substituted succinic anhydride where the polyisobutylene has an Mn ~2000)	78	> 12
D	0.75% Overbased acid of Example 3A 1.0% LZ 2174	80	12
E	0.75% Overbased acid of Example 3A 1.0% PIBSA (Mn ~2000)	81	> 12

As discussed in the background section, it is highly desirable that rheology control agents in this coatings formulation increase Stormer viscosity and sag. The results in Table I clearly demonstrate that the overbased acid of Example 3A in combination with either LZ 2174 or PIBSA achieve this effectively.

5

Table II
Effect of the Overbased Acids and Dispersants in
Hydrocarbon Resin Ink Varnish

	% Resinall 514	% distillates	% Rheology Control Agents	Viscosity @ 26°C	Viscosity @ 60°C
A	50.5	49.5	0	25.73	1.11
B	43	50.7	6.3% Example 13A	67.71	4.57
C	49.6	45.6	4.8% Ircosperse 2176 (an alkenyl succinic anhydride according to this disclosure)	39.75	1.66
D	43.2	46.9	6.2% Example 13A 3.7% Ircosperse 2174 (an alkyl aminoester according to this disclosure)	44.19	16.4
E	42.6	47.3	6.3% Example 13A 3.8% Ircosperse 2176	28.75	7.66

10 The varnishes above were formulated to keep the tack to about 9.6 ± 0.4 @ 400 rpm

The results of example B in Table II indicate that the overbased acid of Example 13A works well as rheology control agent but also increases the viscosity at lower temperatures. Examples D and E of Table II on the other hand, indicate that when the overbased acid is present along with either dispersant Ircosperse 2174 or 2176 the viscosity was greatly reduced at lower temperatures and increased at higher temperatures and clearly demonstrate the invention.

Table III
Effect of Overbased Acids and Dispersants in a Sheetfed Ink Varnish

	% Sylvaprint 4550	% Sylvaprint 6348	% distillates	% Sylvar Alkyd	% Sylfat 9012	% Rheology Control Agents	Viscosity @ 26°C	Viscosity @ 60°C
A	25.5	20.5	37	12	5	0	55.55	1.96
B	22.3	17.5	37.3	11.7	4.9	6.4% Example 13A	170.3	12.32
C	25	20	33	12	5	5.0% Ircosperse 2176	44.26	1.87
D	23	18	34.7	12	5	5.3% Example 13A 2.0% LZ 2174	79.49	4.41
E	20.5	15.8	38.6	10.9	4.5	6.0% Example 13A 3.7% Ircosperse 2176	59.22	7.56

20 The varnishes above were formulated to keep the tack to about 12.7 ± 0.6 @ 400 rpm

Table IV
Effect of Overbased Acids and Dispersants in a Sheetfed Rubine Ink

% Varnish	% Rubine Flush	% Thermol 96 C Wax	Viscosity @ 26 C	Viscosity @ 60 C
60% III-A (baseline)	35%	5%	336.5	2.1
62% III-E (Modified)	35%	3%	145.5	5.71

5

Example 1A.

A reactor is charged with 1725 grams of mineral spirits. The reactor is heated to 32.2°C (90°F), and then 1254 grams (5.75 equivalents) of coconut oil is charged to the reactor. The alcohol 2-methyl-1-propanol (isobutanol; 148 grams; 2 moles) is then charged, followed by water (24 grams; 1.33 moles). Lime (Ca(OH)₂; 223 grams; 6.03 equivalents) is then added and the contents are begun to be stirred. The contents of the reactor are heated to 99° -110°C (210°-230°F) with stirring and held at that temperature until a base number (phenolphthalein) of 4.7-14.1 is reached. The product obtained is saponified coconut oil (calcium carboxylate of coconut acid) in mineral spirits.

15

Example 2A

To the mixture of Example 1A is added 2104 grams of mineral spirits. This cools the reaction mixture to 92°C (200°F). Then carbonation is carried out in seven increments. Each increment of carbonation includes 155 grams (4.19 equivalent) of lime and blowing of carbon dioxide into the reaction mixture. In each increment, the lime is initially allowed to mix thoroughly with the reaction mixture before carbon dioxide is bubbled into the mixture. Carbon dioxide is initially bubbled slowly into the reaction mixture and then the rate is increased. The approximate time for carbonation per increment is 3 hours. About 30 grams of CO₂ is used per hour during each increment. Starting in the second increment and continuing in subsequent increments, 2-methyl-1-propanol (54 grams; 0.73 mole) is charged (this corresponds approximately to 0.35 mole of 2-methyl-1-propanol per mole of water generated in the increment), followed by 155 g of lime and bubbling of carbon dioxide in the manner disclosed in preceding sentences. The carbonation step is repeated in each increment. The mixture is cooled as needed to keep the rate of

bubbling of CO₂ at a maximum while not allowing the overbased calcium carboxylate to freeze. (At a temperature above 95°C, CO₂ simply blows through the reaction mixture and is not absorbed by the lime to produce calcium carbonate, while at a temperature of about 50°C, the overbased calcium carboxylate freezes; it 5 is therefore important to maintain the temperature at about 55-90°C, so that carbon dioxide can be blown at a rate sufficiently high that it can actually be absorbed by the lime while not allowing the overbased carboxylate to freeze). At the end of the seventh and final increment of carbonation, CO₂ is continued to be bubbled to a base 10 number (phenolphthalein) of about 4-7. The temperature at the end of this carbonation procedure is about 70°C. The mixture at this point is an overbased (but not gelled) calcium carboxylate in mineral spirits.

Example 3A

To the mixture of Example 2A is charged 506 grams of 2-methyl-1-propanol and 189 grams of water. The mixture is heated to 82.2°C (180°F). The process is 15 monitored by infrared spectroscopy by monitoring the shift of an absorbance peak from approximately 864 cm⁻¹ to 877 cm⁻¹ indicative of change to crystalline carbonate from amorphous carbonate (conversion from homogeneous overbased carboxylate to overbased carboxylate gel). About 1416 grams of mineral spirits are added when about 80% of total carbonate is converted to the crystalline form (as 20 determined by the IR peaks at 864 and 877 cm⁻¹). Another 2192 grams of mineral spirits are added when 90-100% of the carbonate is converted from the amorphous to the crystalline form. The reaction mixture at this point is a gelled overbased calcium carboxylate.

Example 4A

25 3185 parts of methanol, 28.25 parts of calcium chloride and 226.5 parts of tap water are added to a glass-lined reactor equipped with a heating mantle, thermocouple, metal stirrer, gas inlet tube and condenser. The mixture is heated to 48 °C. with stirring. 644.5 parts of Silo lime (94% calcium hydroxide) are added to the mixture to provide a slurry. The temperature of the mixture is reduced to 45 °C. 30 7075 parts of polypropylene (MW=337) substituted benzene sulfonic acid are added to the mixture over a period of one hour. The temperature of the mixture exotherms

to 46°C. The mixture is stirred for one-half hour. 6275 parts of SC Solvent 100 (a high-boiling alkylated aromatic solvent) are added to the mixture and the mixture is stirred for 15 minutes. Three increments of 1772.75 parts of Silo lime are added to the mixture. Carbon dioxide at a rate of five standard cubic feet per hour is bubbled 5 through the mixture after each increment. Total blowing with carbon dioxide is approximately 10.5 hours with the temperature of the mixture varying from 40°C to 50°C. The mixture is stripped with nitrogen blowing at a rate of two standard cubic feet per hour while heating to reflux over a nine-hour period, the temperature increasing over said period from 47°C to 160°C. The mixture is cooled to room 10 temperature. The mixture is filtered through a Gyro Tester clarifier. The solids content is adjusted to 70% solids with SC Solvent 100. The product is a overbased sulfonate in SC-100.

Example 5A

15,000 parts of the product of Example 4A are placed in a glass-lined reactor 15 equipped with a heating mantle, thermocouple, gas inlet tube, condenser and metal stirrer, and heated to 40°C with stirring. Carbon dioxide is bubbled through the mixture at a rate of one cubic foot per hour for 3.75 hours, the temperature of the mixture varying from 38°C to 46°C during the carbon dioxide blowing. 847.8 parts of isopropyl alcohol, 847.8 parts of methanol and 1304 parts of distilled water are 20 added to the mixture over a five-minute period. The mixture exotherms to 45°C and is then heated to 67°C. 2500 parts of SC Solvent 100 are added to the mixture. The mixture is heated to 78°C and maintained at said temperature for 0.5 hour. The mixture is stripped by bubbling nitrogen at a rate of two standard cubic feet per hour through the mixture over a period of 5.5 hours, the temperature of the mixture 25 increasing from 77°C to 155°C during stripping. The mixture is cooled with cooling water, and 16,700 parts of a gelled product having a solids content of 62.5% by weight are obtained. The product is an overbased sulfonate gel in SC-100.

Example 6A

1200 parts of the product of Example 5A are placed in a resin reactor equipped with a heating mantle, metal stirrer, teflon bearing, gas inlet tube, thermocouple, trap and condenser. 225.5 parts of polypropylene (MW=337) substituted benzene sulfonic acid are added to the mixture over a 10-minute period, and the mixture exotherms to 34°C. The temperature of the mixture is maintained at 34°C for 20 minutes. Water is stripped from the mixture by bubbling nitrogen at a rate of two standard cubic feet per hour through the mixture. The trap is filled with SC Solvent 100 to prevent solvent loss. The temperature increases to 162°C over a two-hour period during stripping. The temperature is then maintained at 162°C for 0.5 hour. 7.5 cubic centimeters of water are collected. The mixture is cooled to room temperature, and 1413 parts of a low oil overbased sulfonate gel with a zero base number are obtained.

Example 7A

15 Distilled tall oil fatty acid, 580 g, is placed in a reactor and combined with 1200 g Stoddard Solvent (a solvent similar to mineral spirits) and 89 g of calcium hydroxide. The mixture is heated with stirring to 95-100°C and held for 1 hour. The mixture is cooled to and maintained at 50-55°C; 100 g of isopropanol and 136 g of calcium hydroxide are added. Carbon dioxide is bubbled into the mixture at the rate of 28 L (1.0 standard cubic feet) per hour for 1 to 1.5 hours until a base number to phenolphthalein of 0-10 is reached. To the mixture are added 100 g of isopropanol and 136 g of calcium hydroxide, and additional carbon dioxide is bubbled into the mixture at the same rate for 1 to 1.5 hours until a base number (phenolphthalein) of 0-10 is reached. Additional 100 g isopropanol and 136 g of calcium hydroxide is added and the mixture similarly carbonated for 1 to 1.5 hours to a base number of 0-10. The mixture is then heated to 160°C to remove the alcohols and water of reaction. The material is cooled to ambient temperature and centrifuged for 1 hour at 1800 rpm to remove impurities. The product obtained is an overbased calcium tallate in Stoddard Solvent.

Example 8A

Four hundred forty-nine g of purified low erucic rapeseed oil is placed in a reaction flask and combined with 692 g of 100 N paraffinic oil, 33 g of glycerin, and 37 g. of calcium hydroxide. This mixture is heated with stirring to 140°C and held
5 at temperature for 4 hours. The material is cooled to 50-55°C; 173 g of isopropanol and 92 g of calcium hydroxide are added. Carbon dioxide is bubbled into the mixture at the rate of 28 L (1.0 standard cubic feet) per hour until a base number (phenolphthalein) of 0-10 is reached. Calcium hydroxide, 92 g, is added and similarly carbonated to a final base number of 0-10. The mixture is heated to 160°C
10 to remove isopropanol and water of reaction. The material is cooled to ambient temperature and centrifuged for 1 hour at 1800 rpm to remove impurities. The resulting product is an overbased calcium rapeseed acid in oil.

Example 9A

Example 8A is substantially repeated except that the 100 N paraffinic oil is replaced by "SC-100", an aromatic solvent approximately equivalent to methyl ethyl benzene. In place of the final heating to 160°C, the mixture is heated to 140°C to remove the isopropanol and water of reaction. After centrifugation, 93 g of SC-100 is added to adjust the material to 51% non-volatile materials. The product is an overbased calcium rapeseed acid in SC-100.
20

Example 10A

Four hundred thirty-six g of purified coconut oil is placed in a reaction flask and combined with 500 g SC-100, 43 g of glycerin, and 89.5 g calcium hydroxide. The mixture is heated with stirring to 140°C and held at temperature for 4 hours. The mixture is cooled to and maintained at 90°C, and 1000 g SC-100 and 100 g isopropanol are added. The temperature is further reduced to 50-55°C. Calcium hydroxide, 132.8 g, is added and carbon dioxide is bubbled into the mixture at the rate of 28 L (1.0 standard cubic feet) per hour for 1-1.5 hours to a phenolphthalein base number of 0-10. Another charge of 132.8 g calcium hydroxide and 100 g isopropanol is added and the mixture is carbonated at the same rate for 1-1.5 hours to the same base number. Finally, another 132.8 g calcium hydroxide and 100 g isopropanol are added and, because of high viscosity, 1000 g of SC-100 is added.
25
30

The mixture is carbonated at the same rate for 1-1.5 hours to the same base number. The mixture is heated to 157°C to remove the isopropanol and water of reaction. The material is cooled to 50°C, 1220 g of SC-100 is added and mixed in for 0.5 hours, and the material is centrifuged for 1 hour at 1800 rpm. The decantate is the 5 product, which is an overbased calcium coconut acid in SC-100.

Example 11A

A reactor is charged with 1063 grams of Exxprint 588D solvent, 763 grams (3.5 equivalents) of coconut oil, 2-methyl-1-propanol (90.6 grams), followed by water (13.8 grams). Calcium hydroxide (142.5 grams; 3.85 equivalents) is then 10 added and the contents are begun to be stirred. The contents of the reactor are heated to about 100°C (212°F) with stirring and held at that temperature until a base number (phenolphthalein) of about 13 is reached. The product at this stage is saponified coconut oil in Exxprint 588D solvent.

Example 12A

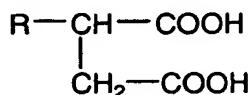
15 To 592 g (1.1 equivalents) of the mixture from Example 11A are added 206 grams of Exx-588D and 76 grams of 2-methyl-1-propanol. Heated the mixture to 80 C and begin adding calcium hydroxide (61.7 grams, 1.67 equivalents). Carbon dioxide (37.4 grams, 1.7 equivalents) was slowly bubbled into the mixture at about 27.8 grams/hour rate over approx. 1.2 hours. This process of adding additional calcium 20 hydroxide and blowing carbon dioxide was repeated two more times at same increments as in Example 2A. The mixture at this point is an overbased calcium coconut acid in Exxprint 588D solvent.

Example 13A

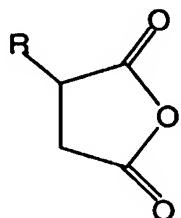
To the mixture from example 12A was charged with 113 g of Exxprint 25 588D, 110 g of isobutanol, 56 g of water and 2.5 g of calcium hydroxide. The mixture was heated to reflux at about 90 C under a blanket of nitrogen for about 195 minutes. The mixture was then heated to about 98°C to strip out isobutanol and water. 393 grams of additional Exxprint 588D was added and the contents were heated to 158 C to remove any residual alcohols or water. The product is overbased 30 and gelled coconut acid in Exxprint 588D.

The Dispersant

The dispersant in this application is a material that is useful to disperse pigments in an oleophilic media. These tend to be low molecular weight emulsifiers or the anhydride or diacid precursor to the emulsifier. A preferred dispersant is a hydrocarbyl substituted succinic acid, its anhydride, or the reaction product of either with an alcohol, an amine, an amino alcohol (hydroxy amine) etc. to make an emulsifier as explained later. The hydrocarbyl substituted succinic acid or anhydride may be represented by the formulae



or



10

wherein in each of the above formulae, R is a hydrocarbyl group of about 8 to about 300 carbon atoms and in one embodiment about 30 to about 200 carbon atoms, and in one embodiment about 12 to about 30 carbon atoms. R can be an alkyl or an alkenyl group. Some of these alkenyl succinic anhydrides are commercially 15 available from companies such as Lubrizol under the trade name Ircosperse®.

In one embodiment, a mixture of at least two hydrocarbyl substituted succinic acids or anhydrides. The hydrocarbyl group R in the above formulae may be derived from an alpha-olefin or an alpha-olefin fraction. The alpha-olefins include 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-eicosene, 1-docosene, 1-triacontene, and the like. The alpha olefin fractions that are useful include C₁₅₋₁₈ alpha-olefins, C₁₂₋₁₆ alpha-olefins, C₁₄₋₁₆ alpha-olefins, C₁₄₋₁₈ alpha-olefins, C₁₆₋₁₈ alpha-olefins, C₁₈₋₂₄ alpha-olefins, C₁₈₋₃₀ alpha-olefins, and the like. Mixtures of two or more of any of the foregoing alpha-olefins or alpha-olefin fractions may be used.

In one embodiment, R in the above formulae is a hydrocarbyl group derived from an olefin oligomer or polymer. The olefin oligomer or polymer may be derived from an olefin monomer of 2 to about 10 carbon atoms, and in one embodiment about 3 to about 6 carbon atoms, and in one embodiment about 4 carbon atoms.

5 Examples of the monomers include ethylene; propylene; butene-1; butene-2; isobutene; pentene-1; heptene-1; octene-1; nonene-1; decene-1; pentene-2; or a mixture of two or more thereof.

In a particularly advantageous embodiment of the invention, the olefin polymers are poly(isobutene)s such as obtained by polymerization of a C_{sub}4 refinery stream having a butene content of about 35 to about 75% by weight and an isobutene content of about 30 to about 60% by weight in the presence of a Lewis acid catalyst such as aluminum chloride or boron trifluoride. These polyisobutenes preferably contain predominantly (that is, greater than about 80% of the total repeat units) isobutene repeat units of the configuration.

15 The hydrocarbyl-substituted carboxylic acids, and anhydrides, and ester and amide derivatives thereof, can be prepared by any of several known procedures which are described in the following U.S., British and Canadian patents: U.S. Pat. Nos. 3,024,237; 3,087,936; 3,172,982; 3,215,707; 3,219,666; 3,231,587; 3,245,910; 3,254,025; 3,271,310; 3,272,743; 3,272,746; 3,278,550; 3,288,714; 3,307,928; 20 3,312,619; 3,341,542; 3,367,943; 3,373,111; 3,374,174; 3,381,022; 3,394,179; 3,454,607; 3,346,354; 3,470,098; 3,630,902; 3,652,616; 3,755,169; 3,868,330; 3,912,764; and 4,368,133. British Pat. Nos. 944,136; 1,085,903; 1,162,436; and 1,440,219. Canadian Pat. No. 956,397. These patents are incorporated herein by reference.

25 One procedure for preparing the hydrocarbyl-substituted carboxylic acids and anhydrides, and ester and amide derivatives is illustrated, in part, in U.S. Pat. No. 3,219,666. This procedure is conveniently designated as the "two-step procedure". It involves first chlorinating an olefin polymer until there is an average of at least about one chloro group for each molecular weight of olefin polymer. (For purposes of this invention, the molecular weight of the olefin polymer is the weight corresponding to the Mn value.) Chlorination involves merely contacting the olefin polymer with

chlorine gas until the desired amount of chlorine is incorporated into the chlorinated polyolefin. Chlorination is generally carried out at a temperature of about 7°C to about 125 °C. If a diluent is used in the chlorination procedure, it should be one which is not itself readily subject to further chlorination. Poly- and perchlorinated and/or fluorinated alkanes and benzenes are examples of suitable diluents.

The second step in the two-step chlorination procedure is to react the chlorinated polyolefin with the alpha-beta olefinically unsaturated carboxylic acid reagent at a temperature usually within the range of about 100 °C to about 200 °C. The mole ratio of chlorinated polyolefin to carboxylic acid reagent is usually about 1:1. (For purposes of this invention, one mole of a chlorinated polyolefin has the molecular weight of a chlorinated polyolefin corresponding to the Mn value of the unchlorinated polyolefin.) However, a stoichiometric excess of carboxylic acid reagent can be used, for example, a mole ratio of 1:2. If an average of more than about one chloro group per molecule of polyolefin is introduced during the chlorination step, then more than one mole of carboxylic acid reagent can react per mole of chlorinated polyalkene. Because of such situations, it is better to describe the ratio of chlorinated polyolefin to carboxylic acid reagent in terms of equivalents. (An equivalent weight of chlorinated polyolefin, for purposes of this invention, is the weight corresponding to the Mn value divided by the average number of chloro groups per molecule of chlorinated polyolefin. An equivalent weight of a carboxylic acid reagent is its molecular weight.) Thus, the ratio of chlorinated polyolefin to carboxylic acid reagent will normally be such as to provide about one equivalent of carboxylic acid reagent for each mole of chlorinated polyolefin up to about one equivalent of carboxylic acid reagent for each equivalent of chlorinated polyolefin with the understanding that it is normally desirable to provide an excess of carboxylic acid reagent; for example, an excess of about 5% to about 25% by weight. Unreacted excess carboxylic acid reagent may be stripped from the reaction product, usually under vacuum, or reacted during a further stage of the process as explained below.

The resulting polyolefin-substituted carboxylic acid or anhydride, or ester or amide derivative, is, optionally, again chlorinated if the desired number of

carboxylic groups are not present in the product. If there is present, at the time of this subsequent chlorination, any excess carboxylic acid reagent from the second step, the excess will react as additional chlorine is introduced during the subsequent chlorination. Otherwise, additional carboxylic acid reagent is introduced during 5 and/or subsequent to the additional chlorination step. This technique can be repeated until the total number of carboxylic groups per equivalent weight of substituent groups reaches the desired level.

Another procedure for preparing hydrocarbyl-substituted carboxylic acids and derivatives of the invention utilizes a process described in U.S. Pat. No. 10 3,912,764 and U.K. Pat. No. 1,440,219. Both of these patents are incorporated herein by reference. According to this procedure, the polyolefin and the carboxylic acid reagent are first reacted by heating them together in a direct alkylation procedure. When the direct alkylation step is completed, chlorine is introduced into the reaction mixture to promote reaction of the remaining unreacted carboxylic acid reagent. 15 According to these patents, 0.3 to 2 or more moles of carboxylic acid reagent are used in the reaction for each mole of olefin polymer. The direct alkylation step is conducted at temperatures of about 180°C to about 250°C. During the chlorine-introducing stage, a temperature of about 160°C to about 225°C is employed.

A preferred process for preparing the hydrocarbyl-substituted carboxylic acids and derivatives of this invention, is the so-called "one-step" process. This 20 process is described in U.S. Pat. Nos. 3,215,707 and 3,231,587. Both of these patents are incorporated herein by reference. Basically, the one-step process involves preparing a mixture of the polyolefin and the carboxylic acid reagent containing the necessary amounts of both to provide the desired hydrocarbyl-substituted carboxylic acids or derivatives of this invention. Chlorine is then introduced into the mixture, 25 usually by passing chlorine gas through the mixture with agitation, while maintaining the mixture at a temperature of at least about 140°C. A variation on this process involves adding additional carboxylic acid reagent during or subsequent to the chlorine introduction. Usually where the polyolefin is sufficiently fluid at 140°C and above, there is no need to utilize an additional substantially inert, normally 30 liquid solvent/diluent in the one-step process. However, as explained hereinbefore,

if a solvent/diluent is employed, it is preferably one that resists chlorination. Again, the poly- and perchlorinated and/or -fluorinated alkanes, cycloalkanes, and benzenes can be used for this purpose.

Chlorine may be introduced continuously or intermittently during the one-step process. The rate of introduction of the chlorine is not critical although, for maximum utilization of the chlorine, the rate should be about the same as the rate of consumption of chlorine in the course of the reaction. When the introduction rate of chlorine exceeds the rate of consumption, chlorine is evolved from the reaction mixture. It is often advantageous to use a closed system, including super atmospheric pressure, in order to prevent loss of chlorine so as to maximize chlorine utilization.

The minimum temperature at which the process is normally carried out is in the neighborhood of 140°C. A preferred temperature range is between about 160 °C and about 220°C. Higher temperatures such as 250°C or even higher may be used but usually with little advantage. In fact, temperatures in excess of 220°C are often disadvantageous because they tend to "crack" the polyolefins (that is, reduce their molecular weight by thermal degradation) and/or decompose the carboxylic acid reagent. For this reason, maximum temperatures of about 200 °C to about 210°C are normally not exceeded. The upper limit of the useful temperature in the one-step process is determined primarily by the decomposition point of the components in the reaction mixture including the reactants and the desired products. The decomposition point is that temperature at which there is sufficient decomposition of any reactant or product such as to interfere with the production of the desired products.

In the one-step process, the molar ratio of carboxylic acid reagent to chlorine is such that there is at least about one mole of chlorine for each mole of carboxylic acid reagent to be incorporated into the product. Moreover, for practical reasons, a slight excess, usually in the neighborhood of about 5% to about 30% by weight of chlorine, is utilized in order to offset any loss of chlorine from the reaction mixture. Larger amounts of excess chlorine may be used but do not appear to produce any beneficial results.

The dispersant can be the reaction product of the reaction between the hydrocarbyl substituted succinic acid or its anhydride with an alcohol, an amine, or an amino alcohol. This product may be an ester or a partial ester when the second reactant is an alcohol. This product may be an amide, imide, salt, amide/salt, partial amide or mixture of two or more thereof when the second component is a polyamine. This product may be an ester, partial ester, amide, partial amide, amide/salt, imide, ester/salt, salt, or a mixture of two or more thereof when component (B) is a hydroxyamine, a mixture of polyol and polyamine, a mixture of polyol and hydroxyamine, or a mixture of polyamine and hydroxyamine. The salt may be an internal salt involving residues of a molecule of the acid or anhydride and the polyamine or hydroxyamine wherein one of the carboxyl groups becomes ionically bound to a nitrogen atom within the same group; or it may be an external salt wherein the ionic salt group is formed with a nitrogen atom that is not part of the same molecule.

During the first reaction step, the first and second components are mixed together and heated at an effective temperature to form the product or a first intermediate. In one embodiment, the temperature is in the range of from about 30°C to about 120°C, and in one embodiment from about 50°C to about 90°C. The reaction time is typically from about 1 to about 120 minutes, and in one embodiment about 1 to about 60 minutes. The components may be dispersed or dissolved in a normally liquid, substantially inert organic liquid solvent/diluent during the reaction. In one embodiment, the components are reacted in amounts sufficient to provide an equivalent ratio of from about 3:1 to about 1:2. In one embodiment, this ratio is from about 1:1 to about 1:2, and in one embodiment about 1:1.4 to about 1:1.9.

During the second reaction step the first intermediate product from the first reaction step is heated at a sufficient temperature to form a second intermediate product with water of reaction being formed. The temperature may be in the range of about 130°C to about 210°C, and in one embodiment about 135°C to about 150°C. The reaction time is typically from about 1 to about 10 hours, and in one embodiment about 1.5 to about 3 hours. When the second component includes a polyol, the second intermediate product comprises one or more bisesters, triesters or

low order (about 2 to about 6, and in one embodiment about 2 to about 4) oligomers containing ester, or ester and acid functionality. When the second component is a polyamine, the second intermediate product comprises one or more bisamides, bisimides, amide/imide, or low order (about 2 to about 6, and in one embodiment about 2 to about 4) oligomers containing amide, imide, amide/imide, acid and/or salt functionality. When the second component is a hydroxyamine, the second intermediate product comprises one or more bisamides, bisesters, ester/amides or low order (about 2 to about 6, and in one embodiment about 2 to about 4) oligomers containing ester, amide, acid and/or salt functionality. When the second component is a mixture of a polyol, polyamine and/or hydroxyamine, the second intermediate product comprises one or more of the above-mentioned products depending upon which polyol, polyamine and/or hydroxyamine is used. During second step a portion of the water of reaction is separated from the second intermediate product using known techniques (e.g., distillation, azeotropic removal of water, molecular sieves, etc.) to provide the desired partially dehydrated product. When first component is a succinic anhydride, the amount of water of reaction that is removed is generally from about 0.2 to about 0.9 moles of water per equivalent of succinic anhydride, and in one embodiment about 0.3 to about 0.8 moles of water per equivalent of succinic anhydride, and in one embodiment about 0.4 to about 0.6 moles of water per equivalent of succinic anhydride. When the first component is a succinic acid, the amount of water of reaction that is removed is generally from about 1.2 to about 1.9 moles of water per equivalent of succinic acid, and in one embodiment about 1.3 to about 1.8 moles of water per equivalent of succinic acid, and in one embodiment about 1.4 to about 1.6 moles of water per equivalent of succinic acid.

The reaction product may be used directly. Alternatively, it may be diluted with a normally liquid organic diluent such as mineral oil, naphtha, benzene, or toluene to form an additive concentrate. The normally liquid organic diluent may be one or more of the precursors or reactants used to make the inventive reaction product, or one or more of the oils or fuels used to make the inventive emulsions described herein.

In one embodiment, the alcohol (e.g. polyol) is a compound represented by the formula



wherein in the foregoing formula, R is an organic group having a valency of m, R is joined to the OH groups through carbon-to-oxygen bonds, and m is an integer from 1 to about 10, and in one embodiment 1 to about 3. The polyol may be a monohydric alcohol, glycol, a polyoxalkylene glycol, a carbohydrate, or a partially esterified polyhydric alcohol. Mixtures of two or more of the foregoing can be used.

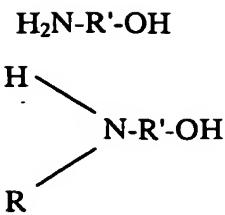
The amine may be aliphatic, cycloaliphatic, heterocyclic or aromatic compound. Examples include alkylene polyamines and heterocyclic polyamines. The alkylene polyamines may be represented by the formula



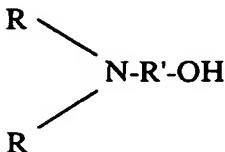
wherein n has an average value between 1 and about 10, and in one embodiment about 1 to about 3, the "Alkylene" group has from 1 to about 10 carbon atoms, and in one embodiment about 2 to about 6 carbon atoms, and each R is independently hydrogen or an aliphatic or hydroxy-substituted aliphatic group of up to about 30 carbon atoms. These alkylene polyamines include ethylene polyamines, butylene polyamines, propylene polyamines, pentylene polyamines, etc.

The hydroxyamine may be a primary, secondary or tertiary amine. The terms "hydroxyamine" and "aminoalcohol" describe the same class of compounds and, therefore, can be used interchangeably. In one embodiment, the hydroxyamine is (a) an N-(hydroxyl-substituted hydrocarbyl) amine, (b) a hydroxyl-substituted poly(hydrocarbyloxy) analog of (a), or a mixture of (a) and (b). The hydroxyamine may be alkanolamine containing from 1 to about 40 carbon atoms, and in one embodiment 1 to about 20 carbon atoms, and in one embodiment 1 to about 10 carbon atoms.

The hydroxyamine may be a primary, secondary or tertiary alkanol amine, or a mixture of two or more thereof. These hydroxyamines may be represented, respectively, by the formulae:



5 and



wherein each R is independently a hydrocarbyl group of one to about eight carbon atoms or hydroxyl-substituted hydrocarbyl group of two to about eight carbon atoms and R' is a divalent hydrocarbon group of about two to about 18 carbon atoms. Typically each R is a lower alkyl group of up to seven carbon atoms. The group -R'-OH in such formulae represents the hydroxyl-substituted hydrocarbyl group. R' can be an acyclic, alicyclic or aromatic group. Typically, R' is an acyclic straight or branched alkylene group such as an ethylene, 1,2-propylene, 1,2-butylene, 1,2-octadecylene, etc. group.

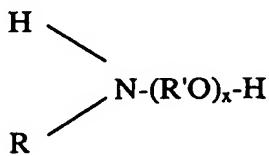
When two R groups are present in the same molecule they can be joined by a direct carbon-to-carbon bond or through a heteroatom (e.g., oxygen, nitrogen or sulfur) to form a 5-, 6-, 7- or 8-membered ring structure. Examples of such heterocyclic amines include N-(hydroxyl lower alkyl)-morpholines, -thiomorpholines, -piperidines, -oxazolidines, -thiazolidines and the like.

The hydroxyamines may be ether N-(hydroxy-substituted hydrocarbyl)amines. These may be hydroxyl-substituted poly(hydrocarbyloxy) analogs of the above-described hydroxy amines (these analogs also include hydroxyl-substituted oxyalkylene analogs). Such N-(hydroxyl-substituted hydrocarbyl) amines may be conveniently prepared by reaction of epoxides with

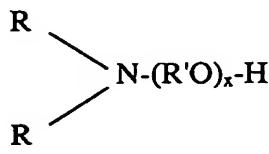
afore-described amines and may be represented by the formulae:



5



10



wherein x is a number from about 2 to about 15, and R and R' are as described above.

Polyamine analogs of these hydroxy amines, particularly alkoxylated alkylene polyamines (e.g., N,N-(diethanol)-ethylene diamine) may be used. Such polyamines can be made by reacting alkylene amines (e.g., ethylenediamine) with one or more alkylene oxides (e.g., ethylene oxide, octadecene oxide) of two to about 20 carbons. Similar alkylene oxide-alkanol amine reaction products can also be used such as the products made by reacting the afore-described primary, secondary or tertiary alkanol amines with ethylene, propylene or higher epoxides in a 1:1 or 1:2 molar ratio. Reactant ratios and temperatures for carrying out such reactions are known to those skilled in the art.

Specific examples of alkoxylated alkylene polyamines include N-(2-hydroxyethyl) ethylene diamine, N,N-bis(2-hydroxyethyl)-ethylene-diamine, 1-(2-hydroxyethyl) piperazine, mono(hydroxypropyl)-substituted diethylene triamine, di(hydroxypropyl)-substituted tetraethylene pentamine, N-(3-hydroxy butyl)-tetramethylene diamine, etc. Higher homologs obtained by condensation of the above-illustrated hydroxy alkylene polyamines through amino groups or through hydroxy groups are likewise useful. Condensation through amino groups results in a higher amine accompanied by removal of ammonia while condensation through the hydroxy groups results in products containing ether linkages accompanied by

removal of water. Mixtures of two or more of any of the aforesaid mono- or polyamines are also useful.

Examples of the N-(hydroxyl-substituted hydrocarbyl) amines include mono-, di-, and triethanolamine, dimethylethanolamine, diethylethanolamine, 5 di-(3-hydroxylpropyl) amine, N-(3-hydroxylbutyl) amine, N-(4-hydroxylbutyl) amine, N,N-di-(2-hydroxylpropyl) amine, N-(2-hydroxylethyl) morpholine and its thio analog, N-(2-hydroxylethyl) cyclohexylamine, N-3-hydroxyl cyclopentyl amine, o-, m- and p-aminophenol, N-(hydroxylethyl) piperazine, N,N'-di(hydroxyl ethyl) piperazine, and the like.

10 Further hydroxyamines are the hydroxy-substituted primary amines described in U.S. Patent 3,576,743 by the general formula



wherein R_a is a monovalent organic group containing at least one alcoholic hydroxy group. The total number of carbon atoms in R_a preferably does not exceed about 20.

15 Hydroxy-substituted aliphatic primary amines containing a total of up to about 10 carbon atoms are useful. The polyhydroxy-substituted alkanol primary amines wherein there is only one amino group present (i.e., a primary amino group) having one alkyl substituent containing up to about 10 carbon atoms and up to about 6 hydroxyl groups are useful. These alkanol primary amines correspond to R_a-NH_2

20 wherein R_a is a mono-O or polyhydroxy-substituted alkyl group. It is desirable that at least one of the hydroxyl groups be a primary alcoholic hydroxyl group. Specific examples of the hydroxy - substituted primary amines include 2-amino-1-butanol, 2-amino-2-methyl-1-propanol, p-(beta-hydroxyethyl)-aniline, 2-amino-1-propanol, 3-amino-1-propanol, 2-amino-2-methyl-1,3-propanediol, 2-amino-2-ethyl-1,3-

25 propanediol, N-(betahydroxypropyl)-N'-(beta-aminoethyl)-pi-perazine, tris-(hydroxymethyl) aminomethane (also known as trismethylolaminomethane), 2-amino-1-butanol, ethanolamine, beta-(beta-hydroxyethoxy)-ethylamine, glucamine, glucoamine, 4-amino-3-hydroxy-3-methyl-1-butene (which can be prepared according to procedures known in the art by reacting isopreneoxide with ammonia), N-3(aminopropyl)-4-(2-hydroxyethyl)-piperadine, 2-amino-6-methyl-6-heptanol, 5-amino-1-pentanol, N-(beta-hydroxyethyl)-1,3-diamino propane, 1,3-diamino-2-

hydroxypropane, N-(beta-hydroxy ethoxyethyl)-ethylenediamine, trismethylol aminomethane and the like.

Hydroxyalkyl alkylene polyamines having one or more hydroxyalkyl substituents on the nitrogen atoms, are also useful. Useful hydroxyalkyl-substituted alkylene polyamines include those in which the hydroxyalkyl group is a lower hydroxyalkyl group, i.e., having less than eight carbon atoms. Examples of such hydroxyalkyl-substituted polyamines include N-(2-hydroxyethyl) ethylene diamine, N,N-bis(2-hydroxyethyl) ethylene diamine, 1-(2-hydroxyethyl)-piperazine, monohydroxypropyl-substituted diethylene triamine, dihydroxypropyl-substituted tetraethylene pentamine, N-(3-hydroxybutyl) tetramethylene diamine, etc. Higher homologs as are obtained by condensation of the above-illustrated hydroxy alkylene polyamines through amino groups or through hydroxy groups are likewise useful. Condensation through amino groups results in a higher amine accompanied by removal of ammonia and condensation through the hydroxy groups results in products containing ether linkages accompanied by removal of water.

In the following examples as well as throughout the specification and in the claims, unless otherwise indicated, all parts and percentages are by weight, all temperatures are in degrees Celsius (°C), and all pressures are at or near atmospheric.

20

Example 1B

A five-liter, four-neck flask fitted with a thermocouple, an addition funnel topped with a N₂ inlet, a Dean-Stark trap topped with a water condenser, and an overhead stirrer is charged with C₁₈₋₃₀ alkenyl succinic anhydride (1740.8 g, 3.71 mol). The contents of the flask are stirred and heated to 64°C. Diethanolamine (590 g, 5.62 mol) is added via the addition funnel over 35 minutes. The mixture undergoes an exotherm to 105°C. The mixture is heated to 140°C over 20 minutes and held at that temperature for 2 hours and 40 minutes. Water of reaction (24 g) is removed. The product has a TAN of 53 mg of KOH/g and a TBN of 53.7 mg of KOH/g.

Example 2B

A five-liter, four-neck flask fitted with a thermocouple, an addition funnel topped with a N₂ inlet, a Dean-Stark trap topped with a water condenser, and an overhead stirrer is charged with C₁₈₋₃₀ alkenyl succinic anhydride (1715 g, 3.66 mol).

5 The contents of the flask are stirred and heated to 50°C. Diethanolamine (653 g, 6.22 mol) is added via the addition funnel over 25 minutes (reaction undergoes an exotherm to 120°C). The mixture is heated to 140°C and held at that temperature for 5 hours. Water of reaction (35 g) is removed. The product has a TAN of 37 mg of KOH/g, and a TBN of 57 mg of KOH/g.

10

Example 3B

A five-liter, four-neck flask fitted with a thermocouple, an addition funnel topped with a N₂ inlet, a Dean-Stark trap topped with a water condenser, and an overhead stirrer is charged with C₁₈₋₃₀ alkenyl succinic anhydride (2133 g, 4.55 mol). The contents of the flask are stirred and heated to 64°C. Glycerol (628 g, 6.83 mol) is added via the addition funnel over 20-25 minutes. The mixture is heated to 150°C over 40 minutes. The temperature of the reaction mixture is increased from 150°C to 170°C over a period of 5 hours and maintained at 170°C for an additional hour. Water of reaction (45 g) is removed. The product has a TAN of 38 mg of KOH/g.

15

Example 4B

A three-liter, four-neck flask fitted with an overhead stirrer, a thermocouple, an addition funnel topped with a N₂ inlet, and a Dean-Stark trap topped with a condenser is charged with C₁₈₋₃₀ alkenyl succinic anhydride (1360.6 g, 2.90 mol). The contents of the flask are stirred and heated to 63°C. Diethanolamine (406 g, 3.87 mol) is added via the addition funnel over 27 minutes. During the addition, the reaction mixture undergoes an exotherm to 114°C. The temperature is increased to 140°C over 15 minutes by external heating, and maintained at that temperature for 45 minutes. Water of reaction (18 g) is removed. The mixture is cooled to room temperature. The TAN of the final product is 60.7 mg of KOH/g.

Example 5B

A two-liter, four-neck flask equipped with a stopcock drain, an overhead stirrer, a thermocouple, an addition funnel topped with a N₂ inlet, and a Dean-Stark trap topped with a water condenser, is charged with C₁₈₋₃₀ alkenyl succinic anhydride (1050.3 g, 2.24 mol). The contents of the flask are heated to 60°C. Triethanolamine (158.7 g, 1.06 mol) and glycerol (293.9 g, 3.19 mol) are added sequentially over a 30-minute period. During the triethanolamine addition, the reaction mixture undergoes an exotherm to 90°C. Upon completion of glycerol addition, the reaction, mixture is stirred and heated to 140°C, and maintained at that temperature for 5 hours to provide the final product which is in the form is a viscous brown liquid. Water of reaction (25 g) is removed. The product has a TAN of 29.3 mg of KOH/g, a TBN of 39.8 mg of KOH/g, and a nitrogen content of 0.98% by weight.

Example 6

A one-liter, four-neck flask fitted with a thermocouple, an addition funnel topped with a N₂ inlet, a Dean-Stark trap topped with a water condenser, and an overhead stirrer is charged with C₁₈₋₃₀ alkenyl succinic anhydride (251.4 g, 0.57 mol) and a mixture of C₁₆ - C₁₈ alpha olefins (140.3 g). The contents of the flask are stirred and heated to 90°C. A polyamine bottoms product corresponding predominately to tetraethylene pentamine (29.6 g, 0.71 mol), is added dropwise via the addition funnel. The mixture undergoes an exotherm to 110°C. The mixture is maintained at 100°C for 3.5 hours. Water of reaction (3.15 g) is removed. The product has a TAN of 49.7 mg of KOH/g.

Example 7B

A one-liter, four-neck flask fitted with a thermocouple, an addition funnel topped with a N₂ inlet, a Dean-Stark trap topped with a water condenser, and an overhead stirrer is charged with C₁₈₋₃₀ alkenyl succinic anhydride (315.6 g, 0.72 mol) and a mixture of C₁₆ - C₁₈ alpha olefins (167.0 g). The contents of the flask are stirred and heated to 90°C. A polyamine bottoms product corresponding predominately to tetraethylene pentamine (30 g, 0.72 mol) is added via the addition funnel over 10 minutes. The mixture undergoes an exotherm to 120°C. The mixture

is maintained at 100°C with stirring for 3.5 hours. Water of reaction (4.0 g) is removed. The product has a TAN of 55.4 mg of KOH/g.

Example 8B

5 A one-pint jar is charged with propylene tetramer substituted succinic anhydride (267 g) and diethanol amine (63 g) and heated to 160°C with stirring over a period of 30 minutes. A nitrogen sparge at a rate of 5 standard cubic feet per hour is used during the heating period. Water of reaction is removed. The color of the liquid mixture changes from lemon-yellow to orange-amber.

Example 9B

10 A one-liter, five-neck flask is charged with propylene tetramer substituted succinic anhydride (296 g), glycerine (96 g) and triethanol amine (176 g). The mixture is heated to 110°C with stirring and a nitrogen purge. The temperature is maintained at 110°C for 1 hour, then heated to 230°C over a period of 3 hours. Water (23 g) is removed. The mixture is cooled to 100°C and filtered.

15 Example 10B

A two-liter, three-neck flask is charged with propylene tetramer substituted succinic anhydride (592 g), glycerine (384 g), toluene (300 ml) and p-CH₃C₆H₄SO₃·H₂O (10 g). The mixture is heated to reflux with stirring and a nitrogen purge (0.05 standard cubic feet per hour) and held at reflux for 3 hours. 20 The temperature increases from 120°C to 135°C during this period. Water (40 g) and toluene (150 ml) are removed. The temperature is cooled to 90°C and a 50% aqueous solution of NaOH (4.3 g) is added dropwise with stirring. The mixture is stirred for 15 minutes. Toluene is stripped from the mixture at 110°C and 15 mmHg. The mixture is filtered.

25 Each of the documents referred to above is incorporated herein by reference. Except in the Examples, or where otherwise explicitly indicated, all numerical quantities in this description specifying amounts of materials, reaction conditions, molecular weights, number of carbon atoms, and the like, are to be understood as modified by the word "about." Unless otherwise indicated, each chemical or 30 composition referred to herein should be interpreted as being a commercial grade material which may contain the isomers, by-products, derivatives, and other such

materials which are normally understood to be present in the commercial grade. However, the amount of each chemical component is presented exclusive of any solvent or diluent oil which may be customarily present in the commercial material, unless otherwise indicated. It is to be understood that the amount, range, and ratio 5 limits set forth herein may be combined. As used herein, the expression "consisting essentially of" permits the inclusion of substances which do not materially affect the basic and novel characteristics of the composition under consideration. For the purposes of this application "consisting essentially of" will exclude the use of water 10 in oil emulsions and oil in water emulsions in the rheology additive, varnish or lacquer, and ink formulation as that would materially affect the rheology of the compositions. It is noted that U.S. 6,172,122 discloses emulsions of gelled overbased substrates with surfactants and aqueous liquids.